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(54) Title: COLORING PIGMENT

(57) Abstract: The invention relates to a method for preparing a coloring pigment, wherein an anionic or cationic clay, which clay contains substantially no agglomerates of clay sheets, is subjected to an ion exchange with an organic dye. The invention further relates to the use of the obtained color pigment for coloring substrates.

WO 01/04216 A1

Title: Coloring pigment

This invention relates to a method for preparing a coloring pigment. This invention further relates to a coloring pigment and the use thereof for coloring substrates.

In the context of the invention, a coloring pigment is understood to mean a substance which can give a particular, desired color to a substrate of another material. In addition to color, a coloring pigment gives coverage and it improves the durability of the substrate, in that a part of the incident light is absorbed and/or reflected. According to the invention, a coloring pigment is therefore distinct from a dye. Although a dye is capable of giving coloring to a substrate, it does not have the other properties mentioned, which a coloring pigment does have.

Polymeric materials are normally colored with inorganic pigments. These provide a good color stability to light, oxygen and heat. As regards color and color intensity, however, these pigments have their limitations. In addition, inorganic pigments are less desirable for environmental reasons. Many inorganic pigments, for instance, contain heavy metals.

Organic pigments not only offer a wider range of color possibilities with higher intensities, but are also broken down faster and better in the environment, for instance under the influence of oxygen. A major disadvantage of organic dyes, however, is that they have a relatively low temperature and UV stability. Moreover, these substances exhibit the tendency to leach out when substrates colored with them are used.

In the literature, attempts to combine the advantages of the known inorganic and organic pigments have already been described. U.S. Patent 3,950,180 discloses a composite material which is based on an organic, basic dye and a mineral, viz. a zeolite or montmorillonite. It has been found, however, that the dye is not very homogeneously distributed over the mineral. Nor can a substrate be colored sufficiently homogeneously with such a composite material.

The international patent application 92/00355 describes a coloring pigment based on a layered double hydroxide and a water-soluble, anionic dye. According to a first possibility, this coloring pigment is prepared by calcination of the layered double hydroxide, so that carbonate ions between the clay sheets are driven out, and subsequent subjection to ion exchange with the dye. According to a second possibility, the layered double hydroxide is formed in situ in the presence of the dye. In the coloring pigment which is obtained according to one of the two possibilities, the dye is also not homogeneously distributed over the clay (the layered double hydroxide). With this coloring pigment, too, a substrate cannot be colored sufficiently homogeneously.

In the international patent application 89/09804, a coloring pigment is described which is based on a combination of a mineral material and an organic pigment. Although the mineral material is broadly defined, the document in fact only shows the use of hectorite. A hectorite slurry is prepared which is heated with stirring for half an hour to 80°C, whereafter an organic pigment in the form of an aqueous solution is added. What is described is that the thus obtained coloring pigment can be used for coloring a variety of materials, such as plastic and rubber compositions. In the examples, only the coloring of polypropylene is shown.

Presently, it has been found that for the coloring of particular materials, such as non-polar materials (polymers) or polar materials (polymers), the coloring pigment described in WO-A-89/09804 is not sufficiently suitable. The coloring pigment proves difficult or impossible to distribute homogeneously in the material to be colored, which results in an unsatisfactory color quality.

It is an object of the invention to provide a coloring pigment which combines the advantages of the known organic pigments with those of the known inorganic coloring pigments, and with which polymeric materials can be colored in an efficient, homogeneous manner. Contemplated is a class of

coloring pigments with which a large number of diverse colors of high intensity can be given to a polymer substrate, which coloring pigments can be broken down properly and fast in the environment. Further, the coloring pigment should be stable under the influence of light, oxygen and heat. It is
5 another object of the invention to provide a coloring pigment which can be incorporated in a homogeneous manner in a large variety of materials to be colored, so that a colored material with an intense color in an optimum color quality is obtained.

Surprisingly, it has presently been found that the stated objects
10 can be achieved by preparing a coloring pigment in a specific manner from an organic dye and a clay. Accordingly, the invention relates to a method for preparing a coloring pigment, wherein an anionic or cationic clay, which clay contains substantially no agglomerates of clay sheets, is subjected to an ion exchange with an organic dye.

15 It has been found that the present method leads to a coloring pigment with a very high intensity. In other words, to obtain the same color intensity as with a coloring pigment from the prior art, a much smaller quantity of coloring pigment can suffice. Further, any color shade can be achieved that can also be created with known organic pigments. Another
20 great advantage of the invention is that the coloring pigment can be incorporated into substrates very well. A very homogeneous color effect is obtained, while substantially no individual coloring pigment particles are perceptible. Leaching out of the coloring pigment does not occur, at least occurs to a much lesser extent than in the known organic pigments.
25 Further, the present coloring pigment is very stable, in comparison with organic dyes, under the influences of light, oxygen and heat, and does not yield any, or hardly any, environmental hazard.

The clay which is used in the present method is an anionic or a cationic clay. In principle, any anionic or cationic clay obtained synthetically
30 or from a natural source can be used. Suitable examples can be selected

from the classes of smectites, hydrotalcites and layered double hydroxides. Particularly preferred are cationic clays, such as sodium or hydrogen montmorillonite, and hydrotalcites.

As already indicated hereinabove, it is an important aspect of the invention that the clay contains substantially no agglomerates of clay sheets. All clay types consist of a sheet structure. Under normal conditions, these sheets form agglomerates, whereby the clay sheets stack onto each other. According to the invention, these agglomerates are to be substantially broken, so that the relative distance between the clay sheets is at least 50 Å, preferably at least 75 Å, and still more preferably at least 100 Å. This distance can be suitably determined using x-ray diffraction techniques.

An example of a suitable procedure for breaking the agglomerates in the clay, i.e., for deagglomeration, is a method whereby the clay is dispersed in, preferably, water that is substantially free of ions. This water preferably has a temperature of 20-60°C. Preferably, the amount of clay is not more than 10% by weight, based on the dispersion, so that the viscosity remains low. This has a positive effect on the processability of the dispersion. Thereafter, the clay is allowed to swell for a period between half an hour and a few hours. Other methods to break the agglomerates in the clay are known to those skilled in the art.

Under certain circumstances, in particular when the coloring pigment to be prepared is to be used for coloring non-polar materials (polymers), it may be desirable to modify the clay and/or the finished coloring pigment.

In this connection, it is noted that according to the invention the classification of a material to be colored into the group of polar or non-polar materials is based on a solubility parameter. This is a parameter in which dispersive and polar properties, as well as the presence of hydrogen bridges, of a material are expressed. According to the invention, when the solubility parameter is 9.5 or higher, a polar material is involved. A solubility

parameter lower than 9.5 is indicative of a non-polar material. For a description of the solubility parameter and how it can be determined, reference is made to the book "Properties of Polymers" by Van Krevelen, 2nd edition, Elsevier, Amsterdam, 1976. For the sake of completeness, solubility parameters of a few materials are presented in Table 1 below.

The modification of the clay to render the coloring pigment contemplated outstandingly suitable for coloring non-polar materials can be carried out by adding to the clay and/or to the finished coloring pigment a surfactant, a block copolymer or a graft copolymer. Although not requisite, it is preferred that the modification be carried out before the clay is subjected to an ion exchange with the dye.

Table 1: Solubility parameters of a few materials

		Solubility parameter
Non-polar polymers	polyethylene	7.7-8.4
	polypropylene	8.2-9.2
	polystyrene	8.5-9.3
Polar polymers	polymethyl methacrylate	9.1-12.8
	polyacrylonitrile	12.5-15.4
	polyvinyl chloride	9.4-10.8
	polyamide 6	12.7
Solvents	hexane	8.2
	chloroform	9.3
	acetone	9.9
	methanol	14.5
	water	23.4

Suitable examples of surfactants are quaternary ammonium compounds, such as octadecylammonium bromide, (ar)alkylsulfonic acids and sulfates, such as dodecyl sulfate, alkylcarboxylic acids, and pyridinium

and phosphonium compounds. The pyridinium and phosphonium compounds preferably possess two non-polar tails bound to a head group. The non-polar tails are preferably alkyl groups which, like the alkyl groups in the other surfactants mentioned, preferably comprise at least six carbon atoms. The alkyl groups will normally not be longer than 24 carbon atoms, although this limit is determined by economic rather than technical motives.

Suitable block and graft copolymers are built up from a hydrophilic and a hydrophobic part. Preferably, they contain two blocks, one of which is compatible with the clay and the other with the material to be colored. The block compatible with clay will typically have a molecular weight of 5,000 or less. The block compatible with the material to be colored will typically have a molecular weight of 20,000 or less. The choice for the two blocks can be suitably made by those skilled in the art on the basis of the nature of the clay and the material to be colored. It has been found that the use of polyethylene oxide blocks is of particular advantage.

The amount of surfactant, block copolymer or graft copolymer will depend on the type of pigment and the substrate to be colored. Normally, this amount will be between 0 and 90, preferably between 5 and 30 mol.%, based on the amount of clay (CEC, see *infra*).

As mentioned, the described modification of the clay is especially advantageous when a non-polar material is to be colored. Examples of non-polar materials where this modification leads to particularly good results are polyolefins, such as polyethylene and polypropylene. It has been found that a surprisingly homogeneous coloring with a high color intensity is achieved.

The clay thus obtained is subjected to an ion exchange with an organic dye which yields the desired color. The organic dye is preferably an ionic dye, so that the ion exchange can be carried out in a simple manner. Examples of suitable dyes are mentioned in Ullmanns Encyklopädie der

technische Chemie, band 11, Verlag Chemie, Weinheim, 1976 under "Farbstoffen" and comprise acridine dyes, anthraquinone dyes, azine (incl. Oxazine and Thiazine) dyes, azo dyes, quinophthalone dyes, natural dyes, formazan dyes, indigo and indigoid dyes, indicator dyes, cationic dyes, leuco vat dyes, methine (including Azomethine) dyes, microscoping dyes, naphtho and benzoquinone dyes, nitro and nitroso dyes, phthalocyanine dyes, reactive dyes, and tri- and diaryl methane dyes. Suitable organic dyes are coloristically divided into the following groups (see Ullman Band 11): direct dyes, developer dyes, oxidation dyes, cationic (basic) dyes, vat dyes, leuco vat dyes, reactive dyes, and acid dyes.

Preferred are cationic and anionic dyes and dyes which can be brought into cationic or anionic form by protonating or deprotonating. These are, for instance, dyes with N^+ , P^+ , S^+ functionalities and/or derivatives thereof. Additionally preferred are dyes with anionic functionalities such as RCO_2^- , $RP(O)O_2^{2-}$ and RSO_3^- , wherein R is defined as an alkyl, aryl or alkylaryl group. Also preferred are dyes having a charge center.

When the coloring pigment to be prepared serves to color a polar material, such as a polar polymer, it is preferred that the dye possesses at least two functional or ionic groups. Examples of such groups are amino groups and acid groups. Dyes that satisfy this criterion are *inter alia* methylene blue and methyl red.

The ion exchange can take place by adding to a dispersion of the clay in warm water, preferably the dispersion described above, a solution of the dye. The dye is preferably dissolved in water in a concentration of between 1% and 50%. The amount of dye that is used in the ion exchange is selected depending on the ion exchange capacity (CEC) of the clay and molar mass and number of reactive groups of the dye. The color shade of the coloring pigment to be prepared can be set by means of the amount of dye. The pH of the dye solution is preferably between 2 and 10, depending on the selected type of clay and the dye, and can be set with suitable buffers.

An advantage of the invention is that the loading of the clay with the dye can be very high. The amount of dye per amount of clay that can be achieved is significantly higher than that which can be achieved with the methods for preparing a coloring pigment based on clay and an organic dye from the prior art. The amount of clay with respect to the amount of dye is
5 preferably selected such that the coloring pigment contains from 2 to 90% by weight, more preferably from 5 to 45% by weight, of pigment.

After the ion exchange, the coloring pigment is preferably washed a few times with water and filtrated. If desired, the material can be dried,
10 for instance in an oven or by spray-drying or freeze-drying, whereafter it can be ground to form a powder to improve processability.

The invention further relates to the use of the coloring pigment obtainable in the above-described manner for coloring substrates. It has been found that the coloring pigment is suitable in particular for coloring
15 substrates of polymeric material. It is possible both to color bulk material and to color a covering layer or coating of a polymeric material. Polymers which have proved to allow of coloring particularly well are polyurethanes, poly(meth)acrylates, polyolefins, such as polyethylene or polypropylene, polyesters and polystyrene. As already described extensively, it is preferred
20 that the coloring pigment further contains a surfactant, a block copolymer or a graft copolymer when non-polar materials are colored. When polar materials are colored, the coloring pigment is preferably based on a dye having at least two functional or ionic groups.

When the present coloring pigment is to be incorporated in a bulk
25 material, it can be added to a melt of the material and/or be homogeneously distributed in the bulk material by means of shearing forces, for instance by extrusion. When the coloring pigment is to be processed into a covering layer or coating, it can be suitably added to the liquid material that is used for forming the covering layer or coating. In a conventional manner, this
30 liquid material can then, after being properly stirred, be applied to a

substrate and cured to form a coating. The substrate in this context can be of all kinds, such as polymer material, ceramic, glass, metal, wood, textile (clothing), and the like. Further, an application of the coloring pigment as a tracer for, for instance, flow profiles is possible by virtue of the small
5 dimensions of the particles of which the coloring pigment consists.

A coloring pigment according to the invention can be distributed very homogeneously over a substrate, so that basically no coloring pigment particles are perceptible. The present coloring pigment therefore unites the properties of a pigment with those of a dye. The fact is that the coloring
10 pigment consists of particles which are smaller than the wavelength of the light. For that reason the coloring pigment can also be designated by the term 'nanopigment'.

The color that can be given to a substrate is uncommonly intense and substantially does not run in any manner. It has further been found
15 that the coloring pigment has a strengthening effect on a substrate. The colored substrate is considerably stabler under the influence of light, heat or oxygen and has improved mechanical properties, such as a greater tensile strength and impact resistance.

The invention will presently be further elucidated in and by the
20 following examples.

Example 1

Ten grams of a montmorillonite clay EXM 757 with a cation exchange capacity of 95 meq./100 g were dispersed in 1 liter of deionized
25 water of 50°C. The clay was allowed to swell for a period of 2 hours, until complete exfoliation had occurred. With x-ray diffraction it was determined that the distance between the clay sheets was 12.1 Å.

The clay thus obtained was subjected to an ion exchange with Methylene Blue (MB). For a complete exchange 3.0 grams of MB were used.
30 This yielded a blue coloring pigment, which was washed, filtrated and

freeze-dried. With x-ray diffraction, it was determined that the distance between the clay sheets was 15.6 Å.

Of this coloring pigment, a Thermal Gravimetric Analysis (TGA) was made using a device suitable for that purpose, obtainable from Perkin Elmer, to be able to compare the thermal stability of the coloring pigment with that of MB per se. The results of this are represented in Fig. 1. In Fig. 1 the line with the symbol \diamond shows the data obtained for pure methylene blue, the symbol \square shows the corrected data obtained for methylene blue in clay, and Δ shows the actual data obtained for methylene blue in clay.

The obtained actual data were corrected for the amount of clay in the sample. Since the clay used contains about 24% MB, this was converted by calculation to an amount of pure MB. It can be seen that the thermal stability of the coloring pigment obtained according to this example is at least 100 K higher than that of pure MB.

Example 1A

0.5 g of the coloring pigment prepared according to Example 1 was mixed with 9.5 g polyethylene powder of high density and a molecular weight of 300,000 g/mole (DOW Chemical Company) in an extruder with a twin screw and a kneading zone and melted at 160°C and processed. The product was a material of a blue color, but had an inhomogeneous distribution of the coloring pigment. A few pigment particles of a size of about 1-20 micrometers were clearly recognizable.

Example 1B

0.5 g of the coloring pigment mentioned in Example 1 was melted and homogeneously mixed in a kneader with a block copolymer comprising a block of polyethylene of a molecular weight of 665 g/mole and a polyethylene oxide block of a molecular weight of 210 g/mole. The material

obtained was subsequently processed with 9.5 g polyethylene powder as described in Example 1A. The resulting product exhibited a remarkably better distribution of the coloring pigment. With the naked eye, no particles were recognizable. An inspection with electron microscopy showed an average particle size in the submicrometer range. The color of the colored polyethylene was virtually identical to the color of the coloring pigment (without polymer).

Example 2

The coloring pigment obtained in Example 1 was used in different coatings (paint):

- a water-based polyether polyurethane coating for concrete;
- a water-based polycarbonate polyurethane coating for metal;
- a water-based polyacrylate coating for metal; and
- an isopropanol-based hybrid silicate coating for scratch protection of steel.

In each coating the coloring pigment was included in three concentrations: 1, 2 and 5% by weight. This was done by dispersing the coloring pigment in the paint using ultrasound activation. After a few hours, a substrate was painted with the coatings and these were cured. The color intensity and homogeneity of the coatings was very high. By light microscopy no inhomogeneities could be observed in the coatings.

Example 3

Ten grams of a montmorillonite clay EXM 757 with a cation exchange capacity of 95 meq./100 g was dispersed in 1 liter of deionized water of 50°C. The clay was allowed to swell for a period of 2 hours, until complete exfoliation had occurred. With x-ray diffraction it was determined that the distance between the clay sheets was 12.1 Å.

The clay thus obtained was subjected to an ion exchange with Methyl Red (MR). For a complete exchange, 2.6 grams of MR were used. This yielded a red coloring pigment, which was washed, filtrated and freeze-dried. With x-ray diffraction, it was determined that the distance
5 between the clay sheets was 23.9 Å.

Example 4

The coloring pigment obtained in Example 3 was used in different coatings (paint):

- 10
- a water-based aliphatic polyurethane coating for concrete;
 - a water-based polycarbonate polyurethane coating for metal;
 - a water-based polyacrylate coating for metal; and
 - a water-based aromatic polyester coating.

In each coating the coloring pigment was included in three
15 concentrations: 1, 2 and 5% by weight. This was done by dispersing the coloring pigment in the paint using ultrasound activation. After a few hours, a substrate was painted with the coatings and these were cured. The color intensity and homogeneity of the coatings was very high. By light microscopy no inhomogeneities could be observed in the coatings.

20 X-ray diffraction spectra were recorded of the coloring pigment per se and of the aromatic polyester coating with 2% by weight of coloring pigment. The coloring pigment showed peaks at 3.69°, 2θ; 7.36°, 2θ. The spectrum of the coating did not show any peaks at those points, which indicates that the clay was nanoscopically dispersed.

25

Example 5

Ten grams of a montmorillonite clay EXM 757 with a cation exchange capacity of 95 meq./100 g was dispersed in 1 liter of deionized water of 50°C. The clay was allowed to swell for a period of 2 hours, until

complete exfoliation had occurred. With x-ray diffraction it was determined that the distance between the clay sheets was 12.1 Å.

The clay thus obtained was subjected to an ion exchange with Methylene Green (MG). For a complete exchange, 4.1 grams of MG were used. This yielded a blue-green coloring pigment, which was washed, filtrated and freeze-dried. With x-ray diffraction, it was determined that the distance between the clay sheets was 15.5 Å.

Example 6

Ten grams of a montmorillonite clay EXM 757 with a cation exchange capacity of 95 meq./100 g was dispersed in 1 liter of deionized water of 50°C. The clay was allowed to swell for a period of 2 hours, until complete exfoliation had occurred. With x-ray diffraction it was determined that the distance between the clay sheets was 12.1 Å.

The clay thus obtained was subjected to an ion exchange with Malachite Green (MaG). For a complete exchange 3.3 grams of MaG were used. This yielded a blue-green coloring pigment, which was washed, filtrated and freeze-dried. With x-ray diffraction, it was determined that the distance between the clay sheets was 22 Å.

Example 7

Ten grams of a montmorillonite clay EXM 757 with a cation exchange capacity of 95 meq./100 g was dispersed in 1 liter of deionized water of 50°C. The clay was allowed to swell for a period of 2 hours, until complete exfoliation had occurred. With x-ray diffraction it was determined that the distance between the clay sheets was 12.1 Å.

The clay thus obtained was subjected to an ion exchange with Brilliant Green (BG). For a complete exchange 4.6 grams of BG were used. This yielded a green coloring pigment, which was washed, filtrated and

freeze-dried. With x-ray diffraction, it was determined that the distance between the clay sheets was 22.7 Å.

Example 8

5 The preparations of the coloring pigments of Examples 1, 3 and 5-7 were repeated with a different clay, viz. a Bentonite with a cation exchange capacity of 85 meq./100 g. The use of this clay, which has larger clay sheets, yielded comparable results with regard to the color intensity.

Example 9

10 Ten grams of a synthetic hydrotalcite ($\text{Mg}_3\text{ZnAl}_2(\text{OH})_{12}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) were dispersed in 1 liter of deionized water of 40°C at a pH of 3. The pH was adjusted with a 5 M HCl solution and checked with pH paper. The clay was allowed to swell for a period of 1 hour until complete exfoliation had
15 occurred.

 The clay thus obtained was subjected to an ion exchange with Methyl Red. This coloring substance was used in a mole ratio of 2:1 with respect to the hydrotalcite. This yielded a yellow coloring pigment, which was washed, filtrated, freeze-dried and ground.

20

Example 10

 Ten grams of a synthetic hydrotalcite ($\text{Mg}_3\text{ZnAl}_2(\text{OH})_{12}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) were dispersed in 1 liter of deionized water of 40°C at a pH of 3. The pH was adjusted with a 5 M HCl solution and checked with pH paper. The clay was
25 allowed to swell for a period of 1 hour until complete exfoliation had occurred.

 The clay thus obtained was subjected to an ion exchange with Fluorescein. This dye was used in a mole ratio of 2:1 with respect to the hydrotalcite. This yielded a red coloring pigment, which was washed,
30 filtrated, freeze-dried and ground.

CLAIMS

1. A method for preparing a coloring pigment, wherein an anionic or cationic clay, which clay contains substantially no agglomerates of clay sheets, is subjected to an ion exchange with an organic dye.
2. A method according to claim 1, wherein the clay has priorly
5 undergone a treatment whereby the agglomerates of clay sheets have been substantially broken.
3. A method according to claim 2, wherein the treatment of the clay consists in dispersing and swelling the clay in water which is substantially free of ions at a temperature between 20 and 60°C.
- 10 4. A method according to any one of the preceding claims, wherein the clay comprises clay sheets, the relative distance between the clay sheets being at least 50 Å.
5. A method according to any one of the preceding claims, wherein the clay is selected from the group of smectites, layered double hydroxides
15 and hydrotalcites.
6. A method according to any one of the preceding claims, wherein the organic dye is selected from the group of acridine dyes, anthraquinone dyes, azine (including Oxazine and Thiazine) dyes, azo dyes, quinophthalone dyes, natural dyes, formazan dyes, indigo and indigoid
20 dyes, indicator dyes, cationic dyes, leuco vat dyes, methine (including Azomethine) dyes, microscoping dyes, naphtho and benzoquinone dyes, nitro and nitroso dyes, phthalocyanine dyes, reactive dyes, and tri- and diaryl methane dyes.
7. A method according to any one of the preceding claims, wherein
25 the dye comprises at least two functional or ionic groups.
8. A method according to any one of the preceding claims, wherein during the ion exchange a surfactant, a block copolymer or a graft copolymer is present.

9. A coloring pigment obtainable in a method according to any one of the preceding claims.
10. Use of a coloring pigment according to claim 9, for coloring a polymeric material.
- 5 11. A polymeric material colored with a coloring pigment according to claim 9.

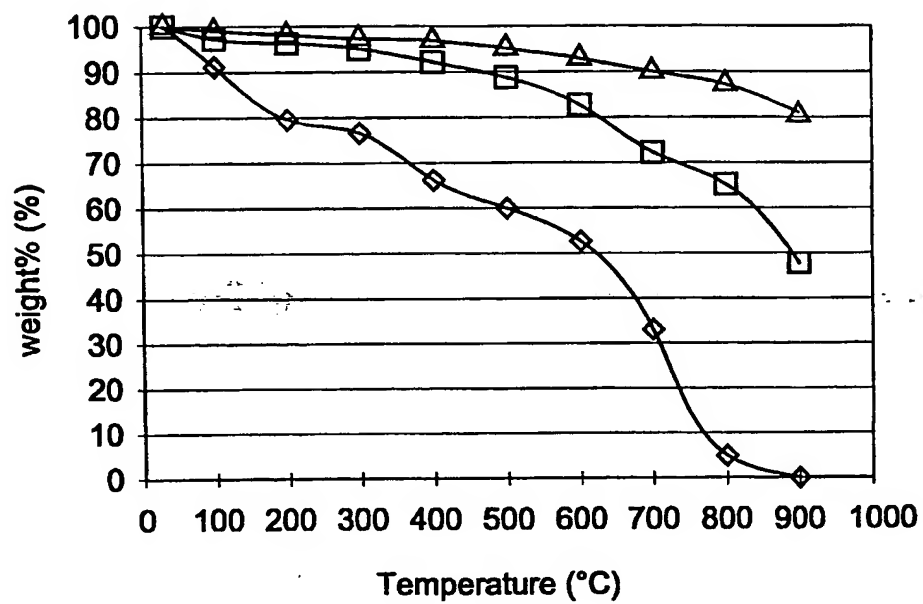


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00480

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B69/02 C09C1/42 C09C3/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 89 09804 A (HUBER CORP J M) 19 October 1989 (1989-10-19) cited in the application page 5, line 22 -page 6, line 10 page 10 -page 13 examples page 7, line 14 -page 8, line 25 page 9, line 18 - line 29</p> <p style="text-align: center;">-/-</p>	<p>1,2,6,7, 9-11</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

A document member of the same patent family

Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/NL 00/00480

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 7546 Derwent Publications Ltd., London, GB; AN 1975-76453w XP002133442 "Pigment preparation - from bentonite and basic dyes" & JP 50 072926 A (MATSUMURA SHOTEN KK), 16 June 1975 (1975-06-16) abstract	1,6,7,9
X	US 3 950 180 A (KATO CHUZO) 13 April 1976 (1976-04-13) cited in the application examples	1,6,7, 9-11
X	WO 92 00355 A (HENKEL KGAA (DE)) 2 January 1992 (1992-01-02) cited in the application claims	1,7,9-11
P,A	WO 00 34379 A (EASTMAN CHEM CO) 15 June 2000 (2000-06-15) page 3, line 25 -page 6, line 16 examples 7-14	1,7,9,10
A	DE 23 38 759 A (BAYER AG) 13 February 1975 (1975-02-13) page 1, paragraph 3 -page 3, paragraph 4; examples	1,3,6,7, 9-11
A	DE 33 01 247 A (MONTEFLUOS SPA) 28 July 1983 (1983-07-28) page 10, line 30 -page 11, line 23 examples	1,6,7,9
A	EP 0 206 800 A (DOW CHEMICAL CO) 30 December 1986 (1986-12-30) examples	1,6,7, 9-11
A	DE 33 29 817 A (SANDOZ AG) 1 March 1984 (1984-03-01) page 4, paragraph 4 -page 6	1,6,7, 9-11
A	EP 0 506 034 A (SONY CORPORATION) 30 September 1992 (1992-09-30) examples	1,6,7
A	EP 0 395 006 A (SONY CORPORATION) 31 October 1990 (1990-10-31) Experimenteele voorbeelden	1,6,7
A	US 4 410 364 A (FINLAYSON CLAUDE M ET AL) 18 October 1983 (1983-10-18) the whole document	1,7,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/NL 00/00480

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 8909804 A	19-10-1989	AU 3449789 A CN 1047682 A EP 0363471 A JP 3500059 T US 5296284 A	03-11-1989 12-12-1990 18-04-1990 10-01-1991 22-03-1994
JP 50072926 A	16-06-1975	NONE	
US 3950180 A	13-04-1976	NONE	
WO 9200355 A	09-01-1992	DE 4020272 A	02-01-1992
WO 0034379 A	15-06-2000	AU 2160600 A	26-06-2000
DE 2338759 A	13-02-1975	NONE	
DE 3301247 A	28-07-1983	IT 1190656 B BE 895626 A CA 1199328 A DE 3348388 C FR 2519994 A GB 2113704 A, B JP 58164643 A NL 8300140 A US 4458073 A	24-02-1988 18-07-1983 14-01-1986 29-05-1991 22-07-1983 10-08-1983 29-09-1983 16-08-1983 03-07-1984
EP 0206800 A	30-12-1986	CA 1265126 A JP 62025170 A US 4840676 A	30-01-1990 03-02-1987 20-06-1989
DE 3329817 A	01-03-1984	FR 2532340 A GB 2126258 A, B IT 1170198 B US 4543128 A	02-03-1984 21-03-1984 03-06-1987 24-09-1985
EP 506034 A	30-09-1992	JP 4299183 A AT 140901 T CA 2063116 A DE 69212516 D DE 69212516 T KR 177929 B US 5516746 A	22-10-1992 15-08-1996 29-09-1992 05-09-1996 06-03-1997 01-04-1999 14-05-1996
EP 395006 A	31-10-1990	JP 2292084 A JP 2770409 B CA 2015615 A DE 69011934 D DE 69011934 T US 5160371 A US 5179065 A	03-12-1990 02-07-1998 28-10-1990 06-10-1994 27-04-1995 03-11-1992 12-01-1993
US 4410364 A	18-10-1983	US 4412018 A CA 1192334 A DE 3145462 A FR 2514776 A GB 2092609 A, B JP 1053706 B JP 1570463 C	25-10-1983 20-08-1985 16-06-1982 22-04-1983 18-08-1982 15-11-1989 25-07-1990

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/NL 00/00480

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4410364 A		JP 58076473 A	09-05-1983
		AU 542170 B	07-02-1985
		AU 7751581 A	27-05-1982
		BE 891142 A	16-03-1982
		BR 8107422 A	10-08-1982
		CA 1166264 A	24-04-1984
		DE 3145423 A	29-07-1982
		DE 3145449 A	29-07-1982
		DE 3145452 A	24-06-1982
		DE 3145456 A	29-07-1982
		DE 3145457 A	09-09-1982
		DE 3145475 A	16-06-1982
		DK 506681 A	18-05-1982
		FI 813616 A,B,	18-05-1982
		FR 2495171 A	04-06-1982
		GB 2088932 A,B	16-06-1982
		GB 2090584 A,B	14-07-1982
		GB 2152109 A,B	31-07-1985
		GR 76347 A	06-08-1984
		IE 52976 B	27-04-1988
		IT 1194108 B	14-09-1988
		JP 1701376 C	14-10-1992
		JP 3057955 B	03-09-1991
		JP 57111371 A	10-07-1982
		LU 83758 A	14-04-1982
		MX 161745 A	20-12-1990
		NL 8105184 A,B,	16-06-1982
		NO 813865 A,B,	18-05-1982
		SE 458768 B	08-05-1989
		SE 8106792 A	18-05-1982
		ZA 8107904 A	27-10-1982